Synthesis and structure investigation of $USiO_4$ - comparison between local structure and bulk

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Synthesis

All experimental procedures were carried out under protective atmosphere in a glove box (N_2, O_2 < 10 ppm). $USiO_4$ was synthesized by adding UCl_4 solution to an excess amount of Na_2SiO_3 solution and adjusting the pH to ~ 8. The green precipitate is centrifuged off and mixed with a $NaHCO_3$ buffer. This slurry is hydrothermally treated at 250 °C, then very slowly cooled down. The obtained product is then washed with distilled water and dried.

Analytical Equipment

X- ray diffraction *D8* by *Bruker AXS GmbH* using Cu Kα, *VarnTec* detector, ($\Delta 2\theta$ = 0.021, 2θ = 15 - 130°, t = 2 s/step).
Confocal micro-Raman Spectroscopy by *Renishaw Raman System (RM-1000)* using a Nd:YAG laser, λ = 532 nm.
FT-IR *EQUINOX 55 TGA-IR* by *Bruker* using KBr pellet, measuring range 400 – 4000 cm^{-1}.
Scanning Elevtron Microscopy using *FEI Quanta 200F,* large-field SE detector, low vacuum mode, with 70 Pa H_2O atmosphere, 30 kV acceleration voltage.
Transmission Electronmicroscopy using *Philips CM300 FEG/UT – STEM* and *FEI Titan 80 – 300 S-TWIN - STEM* with 300 kV acceleration voltage.
EXAFS were measured at the *Rossendorf beamline*, BM-20 (ESRF) employing the UL_{III} - edge at 17185 eV and ThL_{III} - edge at 16310 eV.

Introduction

Coffinite is a natural mineral with general composition $USiO_4$[1]. The structure (SG 141: $I\,4_1/a\,m\,d$) with tetravalent uranium in an eightfold coordination with oxygen and isolated silicate tetrahedra (see fig. 2) is isostructural to zircon, $ZrSiO_4$, and thorite, $ThSiO_4$. Coffinite is the second most important uranium ore. Under reducing conditions with high silica concentrations ($c(SiO_4) \geqq 10^{-4}$ mol/L) the reaction of UO_2 to $USiO_4$ is favoured (**Langmuir's criterion**)[2]. Coffinite therefore may be a potential secondary phase in a deep geological repository for spent nuclear fuel. Estimates on the solubility of coffinite indicate a significantly lower uranium solubility compared to that of UO_2, thus reducing the uranium source term significantly. Unfortunately, reliable and **valdidated thermodynamic data are missing**. However, the use of **natural samples is not feasible**, as these always are associated with significant amounts of impurities like ThO_2, UO_2, selenides, oxides of REE and organic matter. Because of the high α-radiation damage, natural coffinit is also usually amorphous. The **synthesis of coffinite** proves to be **rather challenging**. Recently Pointeau et al.[3] reported the successful synthesis of coffinite by applying the protocol developed by Hoekstra and Fuchs[4]. However, the obtained products always contained amounts of nanocrystalline UO_2.

Fig. 1: Natural coffinite sample

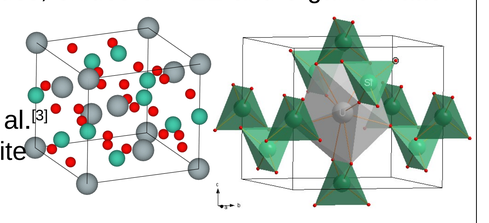


Fig. 2: Unit cell (left) and coordination polyhedra (right) of $USiO_4$

X-ray diffraction

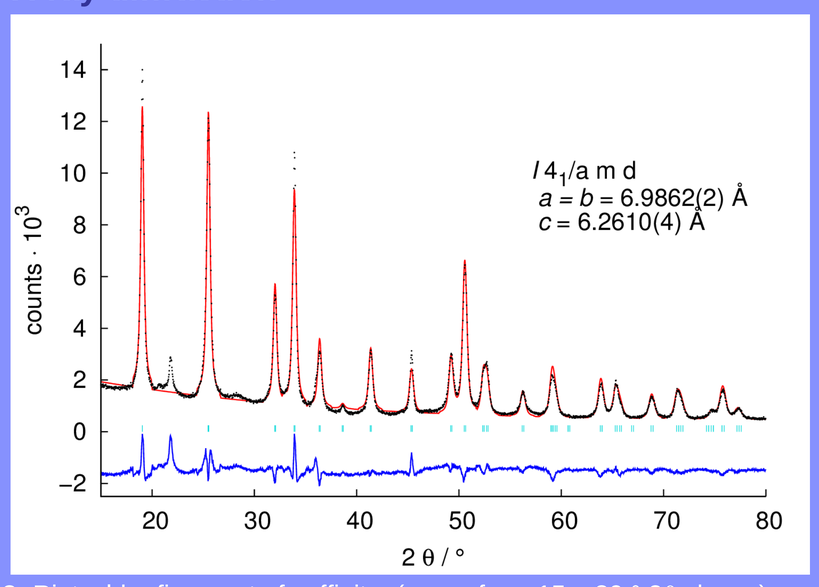


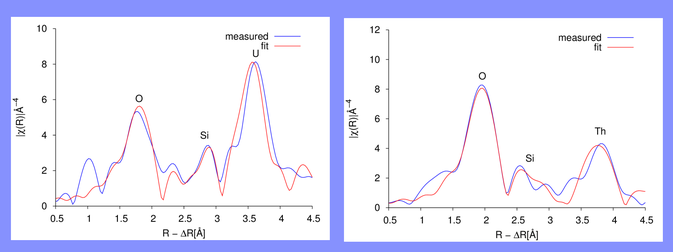
Fig. 3: Rietveld refinement of coffinite (range from 15 – 80 ° 2θ shown). Amorphous silica is visible in the range between 20 – 30° 2θ . The derived lattice parameters are compared to those from literature in Tab. 1.

	Pointeau et al.[3]	Hoekstra & Fuchs[4]	Fuchs & Gebert[5]	This study
a = b	7.0135(4)	6.981(4)	6.995(5)	6.9862(2)
c	6.2669(6)	6.250(5)	6.263(4)	6.2610(4)

Tab. 1: Comparison between obtained lattice parameters from rietveld refinement and in literature.

EXAFS

Fig . 5: k^3 weighed FT-magnitudes of EXAFS measurements (blue) and fit (red) of coffinite (left) and thorite (right), range shown up to 4.5 Å.



The obtained bond lenghts are compared to those from XRD in tab 2.

Bond distances [Å]	Coffinite		Thorite	
	XRD	EXAFS*	XRD	EXAFS*
M-O_1	2.276(1)	2.27	2.3499(4)	2.34
M-O_2	2.407(1)	2.39	2.4695(6)	2.44
M-Si_1	3.1304(2)	3.13	3.140(1)	3.18
M-M_1	3.8277(1)	3.83	3.9130(7)	3.92
M-M_2	5.8524(2)	5.84	5.914(1)	)*

*Errors in distances are ± 0.02 Å.
)* signal for Th-Th_2 distance was very weak and resulted in a bad fit but could be estimated within 5.87 – 5.96 Å.

Tab. 2: Comparison between bond distances calculated from rietveld refinement and obtained from Th L_{III} / U L_{III} – edge by EXAFS in coffinite and thorite.

SEM

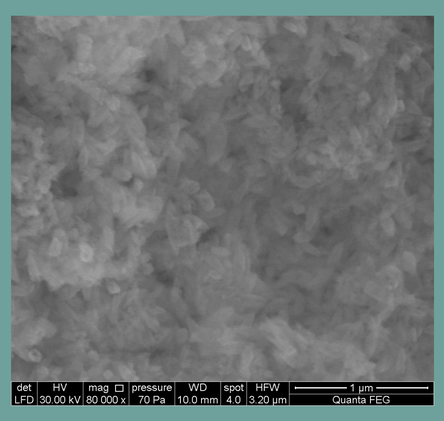


Fig . 4: SEM image of coffinite, showing the lentil like morphology of the synthesized particles.

TEM

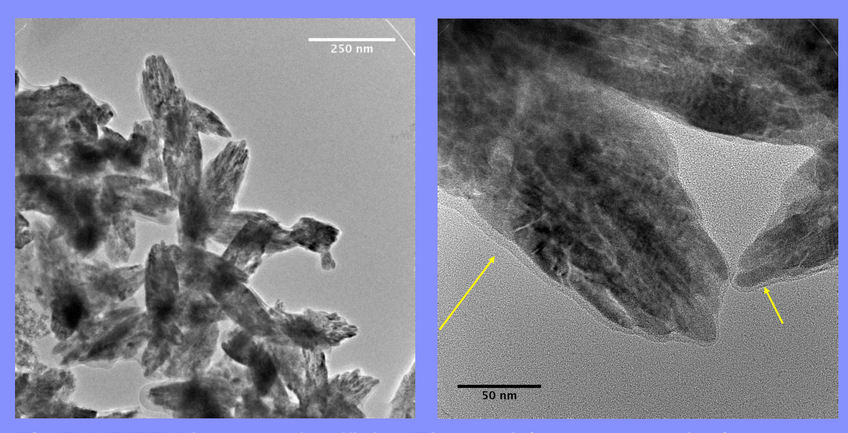


Fig.5: HRTEM images of coffinite. The particles appear to be large agglomerates of smaller particles, which are covered in an amorphous silicate layer (see arrows, right).

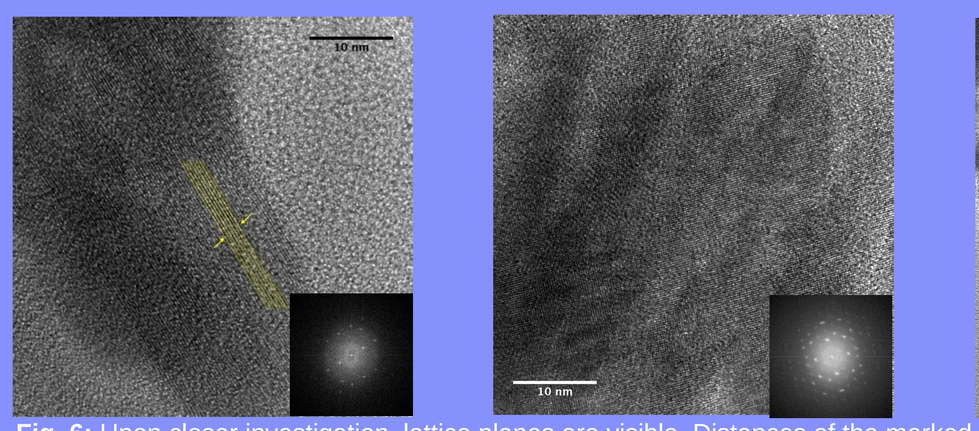


Fig. 6: Upon closer investigation, lattice planes are visible. Distances of the marked planes correspond to $d_{(200)}$ = 0.34 nm (left). Tetragonal symmetry is clearly visible in the FFT (middle, inset). View of particles along four-fold axis (right). Lattice planes $d_{(200)} = d_{(020)}$= 0.34 nm and $d_{(220)}$ = 0.25 nm are visible.

IR

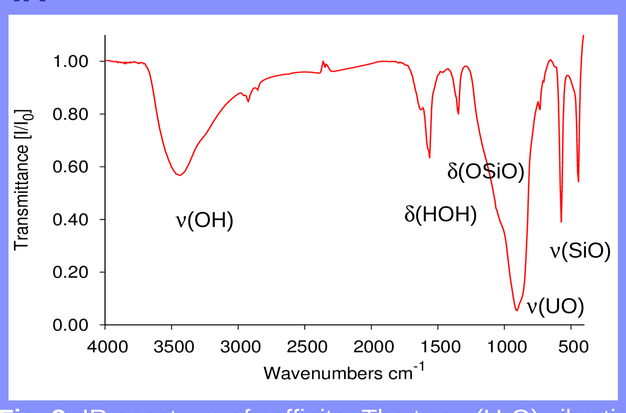


Fig. 8: IR spectrum of coffinite. The two ν(U-O) vibrations are very close. Also significant water signals (3300 cm^{-1} - 3000 cm^{-1}) can be observed.

Raman

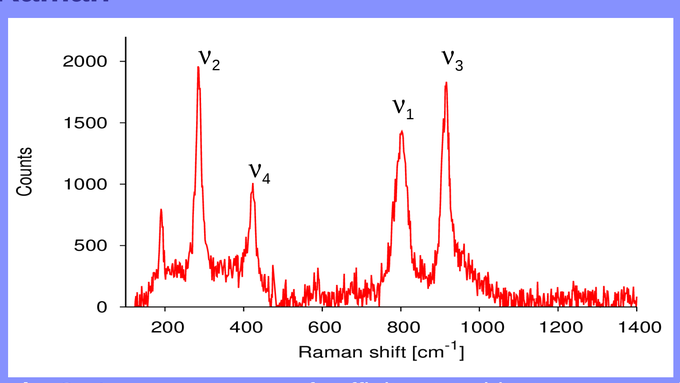


Fig. 9: Raman spectrum of coffinite at ambient pressure. The observed frequencies are mainly modes from the SiO_4-tetrahedron and correspond to those in zircon [6] and thorite [7].

Conclusion

- In contrast to other recent studies [3,8] we were able to **synthesize coffinite, $USiO_4$, without impurities of UO_2.**
- Bond leghts of $USiO_4$ measured with **EXAFS and calculated from Rietveld refinemen**t are in very **good agreement**.
- Raman data of $USiO_4$ has been collected for the first time. The spectrum shows strong resemblance to those of $ThSiO_4$ and $ZrSiO_4$.
- SEM and HRTEM imaging show that $USiO_4$ forms agglomerated nm-sized crystals with the general morphology similar to $ThSiO_4$ [9].

Outlook

- High pressure-Raman investigation ongoing.
- Currently synthesis and characterisation of $U_xTh_{(1-x)}SiO_4$ solid solutions to study the behavior of lattice parameters, properties.
- IR spectroscopy shows significant „water“ content. Role of hydroxyl groups and/or water in the structure still to be determined. - Same effect on lattice parameter as in $ThSiO_4$? [10]

References

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